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(54) Title: HEAT-SEAMABLE THERMOSET SHEETING MEMBRANE AND METHODS OF MANUFACTURING AND USING SAME

(57) Abstract

Disclosed is a method for producing a heat-seamable, thermoset elastomeric matrix, the method comprising: (1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while (2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a vulcanizable elastomeric matrix, and (3) curing the thermoplastic-containing matrix, thereby producing the heat-seamable, thermoset elastomeric matrix.

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HEAT-SEAMABLE THERMOSET SHEETING MEMBRANE AND METHODS OF MANUFACTURING AND USING SAME

Technical Field Of The Invention

Our present invention is directed to a weatherable, heat-seamable novel thermoset sheeting membrane as well as to waterproof liners and coverings made from our novel sheeting membrane. Another aspect of our invention is directed to our preferred method for providing a roof with a waterproof covering, utilizing our novel thermoset sheeting membrane.

Our novel thermoset sheeting membrane can preferably be prepared advantageously from EPDM terpolymer elastomer and an olefinic polymer additive. ("EPDM" is the abbreviation for a terpolymer elastomer made from ethylene-propylene diene monomer.) The inclusion of a particularly preferred polymer additive, such as high density polyethylene, enables the heat-seaming of overlapping edge margins of cured adjacent thermoset membrane sheets, resulting in superior adhesion therebetween.

Background Of The Invention

With respect to industrial flat-roofing applications, the modern trend is toward membrane roofing and away from built-up asphalt roofing.

Indeed, membrane roofing offers several distinct advantages over traditional built-up asphalt roofing. Advantages include increased safety for the applicator of the roofing components, easier installation, increased resistance of roofing materials to "cold cracking," and protection against leaks over an extended period of time.

Additional uses for our novel heat-seamable thermoset sheeting membrane (as a waterproof membrane) are in connection with municipal water-storage tanks (and other vessels) as well as reservoirs, irrigation channels, canals, recreational ponds including golf course water hazards, and industrial waste-water treatment facilities including settling ponds.

It is desirable, for a number of reasons — especially protection of the environment — that sheeting membrane for uses of this sort possess enough structural integrity as to ensure against undesired water seepage.

Various elastomeric membranes, especially vulcanized EPDM, have been widely used for these sorts of applications.

Vulcanized EPDM membrane is known to possess such desirable physical properties as high strength, excellent elongation, satisfactory cold-flexibility properties, and general resistance to outdoor weathering.

Sheets are typically seamed with commercially available adhesives.

While years of commercial experience suggest that sheet-seaming generally provides an excellent roofing system, the seam is occasionally the weak link, in that membrane failure usually occurs at a seam. Roofing manufacturers are constantly working to improve this part of the roofing system. Our invention will provide a greater seam-bond strength and reduce seam delamination.

Some prior attempts to achieve successful bonding between elastomeric membrane layers are set forth in U.S. Patent No. 5,162,436 to Davis et al., wherein certain so-called "self-adhering" heat-seamable sheet material for roofing is disclosed. Such sheet is said to be prepared from an uncured polymeric composition-of-matter.

In U.S. Patent No. 5,093,206 and 5,096,743 (both to Schoenbeck) as well as in U.S. Patent No. 4,461,875 to Crepeau — roofing membrane is disclosed. The membrane, initially uncured, is cured on the roof.

In European Patent Application 0 143 131/A1 to Bridgestone Tire Company Limited, there is disclosed a water-proofing sheet that is formed from a composition which includes a partially-cured thermoplastic.

However, those skilled in the art are generally familiar with the various sorts of difficulties which can arise from utilizing roofing membranes and systems that rely upon cure-in-place procedures.

Disclosed in U.S. Patent No. 4,767,658 to Lorenz are fully-cured thermoset ethylene-propylene rubber sheets having integral thermoplastic adhesive strips. In the '658 Lorenz patent, the thermoplastic adhesive strips, which are molded along the lateral edge margins of the cured thermoset rubber sheets, are manufactured utilizing a procedure whereby

the thermoplastic strips are applied to the edge margins of the uncured thermoset ethylene-propylene rubber sheets prior to vulcanization of the rubber sheeting. The strips are used to bond ethylene-propylene sheets together in an overlapping splice.

Disclosed in U.S. Patent No. 4,778,852 to Futamura is a roofing composition "blend," said to include two principal ingredients, namely a so-called "blocked" thermoplastic elastomer and a vulcanized elastomer.

In particular, the disclosed thermoplastic elastomer is said to be made up of both crystalline and amorphous "blocks" or regions.

Objects Of The Invention

Heat-seamable sheeting which enables the formation of water-tight seams possessing superior strength is highly desirable. Any seam thus formed, moreover, must be of sufficient strength as to resist both short-term and long-term stresses as well as oxidation, hydrolysis, and other chemical attack. Long-term stresses can be caused by roof movement, strong winds, freeze-thaw cycles, etc., as well as oxidation.

It would further be desirable that a roofing system be relatively easy to set-up and maintain, and possess a significantly long useful life.

Additional objects — which our present invention meets — are set forth in greater detail hereinbelow.

Summary Of The Invention

Briefly stated, one aspect of our present invention is directed to a method of making a thermoplastic-containing, cured elastomeric matrix, as well as to the thermoplastic-containing, cured matrix which results.

Yet another aspect or feature of our present invention is directed to a method of heat-seaming together adjacent sheets of the thermoplastic-containing, cured elastomeric matrix, and to the thermoplastic-containing, cured and heat-seamed elastomeric matrix thus produced.

Accordingly, our present invention, succinctly stated, is directed to a method for producing a heat-seamable, cured elastomeric matrix.

Our preferred method for producing a heat-seamable, cured

elastomeric matrix, more particularly stated, comprises (1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a heterogeneous dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while (2) heating the heterogeneous dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a vulcanizable elastomeric matrix.

Another aspect of our invention is directed to the thermoplastic-containing, vulcanizable elastomeric matrix that is produced as a result of employing this method. The vulcanizable, thermoplastic-containing matrix is subjected to heat and pressure sufficient to cure the elastomeric matrix.

Our preferred method of joining together edge margins of separate sheets of the cured, thermoplastic-containing elastomeric matrix material described above comprises overlappingly contacting edge margins of adjacent sheets of the thermoplastic-containing, cured elastomeric matrix material and next subjecting the overlappingly contacting edge margins of the elastomeric matrix sheets to heat and pressure sufficient to bond the contacting edge margins of the adjacent sheets together, for purposes of providing a water-tight joint therebetween.

Other aspects, features, and advantages of our present invention are discussed in greater detail hereinbelow.

Industrial Applicability

One use of our invention is as a heat-sealable thermoset sheeting membrane, while another use is as a waterproof covering made from such a sheeting membrane.

In particular, uses for our sheeting membrane as a waterproof membrane are contemplated as being utilized in connection with municipal water-storage vessels and reservoirs, canals and irrigation channels,

recreational ponds including golf course water hazards, and industrial waste-water treatment facilities including settling ponds and lagoons.

Such a membrane may be made from a thermoset elastomer, especially EPDM, advantageously formulated with from about 3 to 75 phr, preferably 5 to 50 phr, of thermoplastic polymeric material, the presence of the thermoplastic polymeric material thereby enabling the membrane to be heat-sealable. The result is superior adhesion of the membrane plies —together— at room temperature and at elevated temperatures of 70 °C.

Such a membrane utilizes certain advantages of a thermoset elastomer, such as vulcanized EPDM, while at the same time enabling the obtaining of water-tight heat-sealed bonds between the membrane plies without the use of separately applied adhesive.

In particular, it is contemplated that the presence of the EPDM would provide such a membrane with desirable cold flexibility properties, superior strength, as well as significant resistance to outdoor weathering when exposed to natural elements.

Such a "self-adhesion" capability — for the thermoset membrane of our present invention — is unique for thermoset membranes, in that the membrane has the potential of including an integral seam of superior bond strength.

It is further contemplated that the protective membrane of our present invention will prove itself useful as "roof flashing," in that our membrane can readily be made to follow irregular contours of structures, such as chimney tops, typically randomly located atop roofs.

Moreover, when used as a roof covering, the composition of this invention — when used in membrane form or otherwise — may cover any roofing base material, such as wood, composition board, concrete, brick or metal. In many applications, insulating or vapor barrier layers may be first placed over the roof prior to the positioning of the composition of this invention upon the roof. (It is to be understood, however, that any such presence of insulation layers is not essential to this invention.)

Detailed Description Of Invention

In the ensuing detailed description, certain terms will be utilized for purposes of conciseness and otherwise to elucidate the various features and advantages of our present invention. These terms are defined below.

Definitions Of Terms Used Herein

The term "ambient temperature" is understood to mean the temperature of the environment in which an experiment is conducted or in which any physical or chemical event occurs.

The term "cure" is understood to mean the crosslinking of a crosslinkable polymer by any means.

The term "elastomer," as originally defined in the 1940s referred to synthetic, thermosettable so-called "high polymers" having properties similar to those of vulcanized natural rubber, namely, the ability to be stretched to at least twice their normal length and to retract very rapidly to approximately their original length when released. Included among the more widely-known elastomers introduced since the 1930s are styrene-butadiene copolymer; polychloroprene (also known as "neoprene"); nitrile rubber; butyl rubber; polysulfide rubber; *cis*-1,4-polyisoprene; ethylene-propylene copolymers as well as terpolymers (such as EPDM rubber); silicone rubber; and polyurethane rubber. These can be crosslinked with sulfur, peroxides, or other suitable crosslinking agents.

The term "elastomer" was subsequently extended — beyond the definition provided immediately above — by those practicing the art, to include uncrosslinked polyolefins that are thermoplastic; and these are generally known as "TPO rubbers." Their extension and retraction properties are notably different from those of thermosetting polymers, but they are well adapted to such specific uses as wire and cable coating, automobile bumpers, vibration dampers, as well as a wide assortment of specialized mechanical products.

The term "matrix" as used herein shall mean a composition-of-matter which includes at least one component or ingredient of interest.

The term "melting temperature" as used herein is understood to mean that temperature range at which a crystalline polymeric material undergoes a phase change.

The term "membrane" as used herein shall mean a special sort of "matrix," in that a "membrane" is a polymeric sheet or film of generally planar shape and substantially uniform thickness, wherein the membrane includes at least one component or ingredient of interest.

The term "phr" is understood to mean parts by weight of a specific component or ingredient of interest per hundred parts by weight of rubber used in the formulation.

The term "pli," used in connection with adhesion (in general) or an adhesive bond (in particular), means "pounds per linear inch."

The term "psi," as used in this specification to refer to pressure or shear stresses, is understood to mean "pounds per square inch."

The term "room temperature" means 25 °C (77 °F).

The term "softening temperature" is understood to mean that temperature range at which a polymeric material ceases to possess such physical properties as hardness, stiffness and brittleness.

A "thermoplastic polymer" is one that is able to be repeatedly (1) softened by heating and (2) hardened by cooling, through a characteristic temperature range. A thermoplastic polymer, when in the softened state, can be made into various articles by such "forming" or "shaping" steps as —for example— calendering, molding, stretching or extruding.

A "thermosetting polymer" is one that is capable of being changed into a substantially intractable or infusible (i.e. insoluble) product, upon being cured by heat or other means.

The term "vulcanization" is understood to mean a physicochemical change which results from the cross-linking of the unsaturated hydrocarbon chain of natural rubber, polyisoprene, EPDM, etc. with sulfur, usually with application of heat. The overall effect of vulcanization is to convert a rubber-like hydrocarbon from a soft, tacky, thermoplastic

to a strong, temperature-stable thermoset having unique elastic modulus and yield properties.

Additional terms are defined throughout this patent specification.

As was briefly mentioned above, one aspect of our invention, succinctly stated, is directed to a process or method for producing a thermoplastic-containing, heat-seamable, cured elastomeric matrix.

Our preferred method for producing a heat-seamable, cured elastomeric matrix, more particularly stated, comprises

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to melt and become dispersed throughout the elastomeric material, thereby producing a vulcanizable elastomeric matrix.

Throughout this specification, we use the term "softening/melting" temperature, because the thermoplastic polymeric materials disclosed in this specification generally consist of crystalline polymeric material as well as amorphous polymeric material, wherein the crystalline polymeric material has a characteristic melting temperature range and the amorphous polymeric material has a characteristic softening temperature range.

Yet another aspect of our present invention is directed to the thermoplastic-containing, vulcanizable elastomeric matrix which is produced as a result of employing our method, briefly noted above.

The vulcanizable, thermoplastic-containing matrix which results is subjected to heat and pressure sufficient to cure the elastomeric matrix.

Our preferred method of joining together edge margins of separate

sheets of the cured, thermoplastic-containing elastomeric matrix material described above comprises overlappingly contacting edge margins of adjacent sheets of the thermoplastic-containing, cured elastomeric matrix material and next subjecting the overlappingly contacting edge margins of the elastomeric matrix sheets to heat and pressure sufficient to bond the contacting edge margins of the adjacent sheets together, for purposes of providing a water-tight joint therebetween.

Still more particularly, yet another aspect of our present invention is directed to a compoundable (i.e. mixable) polymeric composition-of-matter comprising vulcanizable elastomeric material and thermoplastic polymeric material, and optionally including such traditional rubber additives such as "carbon black" fillers, various mineral fillers, plasticizers (such as mineral oils), curatives (such as sulfur), as well as certain "processing" ingredients which are used to aid in mixing, molding, extruding, calendering, or stabilizing an intermediary or ultimate elastomeric matrix product.

In the case of our present invention, the thermoplastic polymeric material is added to the rubber-containing compoundable mixture of ingredients before cure, the ingredients being mixed to make the desired compound, whereupon the compound can be shaped into sheet-like membranes, and — if so shaped — subsequently cured, to enable secure heat-seaming of the membrane to itself after application of the membrane to a roof or other surface.

Crystalline/amorphous thermoplastic polymeric material of suitable melting/softening temperature range is preferred.

In particular, if the melting/softening temperature value is too high — greater than about 232 °C (ca. 450 °F) for example — those skilled in the art will generally agree that it is difficult to satisfactorily heat-seam at field conditions; and if the melting/softening temperature value is too low — e.g. 93 °C (ca. 200 °F) — the roof surface ambient temperatures during summer months could cause seam failure. Anyone skilled in this

particular art is readily able to determine which plastic resin to use in a specific application.

Accordingly, the thermoplastic polymer material preferably has a melting/softening temperature range of about 35 °C to about 140 °C and is about 35 % to 100 % crystalline, based on weight. The remainder of the thermoplastic polymer material is amorphous.

For purposes of providing a complete disclosure, suitable vulcanizable elastomeric material — for purposes of our present invention — includes but is not limited to chlorinated polyethylene; ethylene/acrylic; isoprene-acrylonitrile; polybutadiene; polyisobutylene; styrene-butadiene copolymer; polychloroprene (also known as "neoprene"); nitrile rubber; butyl rubber; polysulfide rubber; *cis*-1,4-polyisoprene; ethylene-propylene terpolymers (such as EPDM rubber); silicone rubber; and polyurethane rubber; as well as combinations (or "blends") of these.

In particular, and as is disclosed in U.S. Patent No. 4,778,852 to Fatamura, we prefer that the diene monomer which is utilized in forming the EPDM terpolymer be a non-conjugated diene. Examples of suitable non-conjugated dienes include but are not limited to dicyclopentadiene; alkyldicyclopentadiene; 1,4-pentadiene; 1,4-hexadiene; 1,5-hexadiene; 1,4-heptadiene; 2-methyl-1,5-hexadiene; 1,4-octadiene; 1,7-octadiene; 5-ethylidene-2-norbornene; 5-(2-methyl-2-butenyl)-2-norbornene; and cyclooctadiene.

Fillers suitable for inclusion in the compoundable polymeric matrix of our invention include but are not limited to carbon black, ground coal, calcium carbonate, clay, silica, cryogenically ground rubber, and the like.

Carbon black may advantageously be used in an amount ranging from about 20 phr to about 300 phr.

Any such carbon black that is used may, for example, be selected from general purpose furnace ("GPF"), fast extrusion furnace ("FEF"), or semi-reinforcing furnace ("SRF") commercially available carbon black.

Suitable processing materials include oils, waxes, and the like.

Mineral oils are the preferred processing materials that are used in compoundable polymeric matrices which contain EPDM, with naphthenic and paraffinic oils being most preferred.

Such processing materials may advantageously be included in the compoundable polymeric matrix in an amount ranging from about 10 phr to about 300 phr, and preferably in an amount ranging from about 20 phr to about 150 phr, based upon EPDM.

Also optionally included in the compoundable polymeric matrix or composition-of-matter are inorganic or mineral fillers such as talc, mica, clay, silicates, and whiting. Fillers of these sorts may advantageously be included in the compoundable polymeric matrix or composition-of-matter in an amount ranging from about 10 phr to about 150 phr.

Like amounts of other conventional agents such as zinc oxide, stearic acid, anti-oxidants, anti-ozonants, flame retardants, and the like may advantageously also be optionally included in the above recipe.

Any curing systems, including peroxides, could potentially be used. Sulfur curatives are generally preferred.

Sulfur, preferably in elemental form, such as the commonly used "rhombic" crystalline form (called rubber makers' sulfur or spider sulfur), provides optimal tensile, tear, and cure characteristics to the cured rubber composition.

Sulfur curative may thus advantageously be used in amounts ranging from about 0.3 phr to 2 phr.

The thermoplastic-containing, vulcanizable elastomeric matrix of our invention may optionally further include a cure accelerator such as a thiazole or a thiuram monosulfide. Suitable thiazoles include but are not limited to thiuram monosulfides and disulfides, benzothiazyl disulfide, and 2-mercaptobenzothiazole.

The thermoplastic-containing, vulcanizable elastomeric matrix of our present invention may further optionally include a dithiocarbamate-type accelerator, such as a salt of a dialkyldithiocarbamate, wherein any

alkyl groups may advantageously have from 1 to 6 carbon atoms and any such salt may advantageously be formed with bismuth, cadmium, copper, iron, lead, potassium, selenium, sodium, tellerium or zinc.

Other optional ingredients such as activators, anti-degradants, tackifiers, and the like are to be considered as forming a part of our present invention — if incorporated into our thermoplastic-containing, vulcanizable elastomeric matrix.

Furthermore, the compounding of the composition of this invention may be accomplished by any suitable means including an internal mixer, a two-roll mill, a transfer mixer, as well as an extruder.

Our present invention is thus not dependent upon any particular apparatus that is utilized to effect any method disclosed herein.

In one preferred embodiment of our present invention, a high density polyolefin is first compounded with a vulcanizable elastomeric material, and the compounded mixture is next processed or formed into the shape of a sheet-like membrane. The vulcanizable, thermoplastic-containing membrane is then cured. Thereafter, edge margins of separate thermoplastic-containing sheet-like membranes, each cured thusly, can advantageously be overlappingly contacted and heat-seamed together, for purposes of providing a water-tight seal therebetween.

A particularly preferred polyolefin material used to promote adhesion in our invention is high density polyethylene ("HDPE").

The above-recited ingredients can advantageously be combined and subsequently compounded utilizing equipment such as an internal mixer, a two-roll mill, an extruder, a "Banbury" mixer, or any other mixer suitable for forming a viscous, relatively uniform admixture.

The resulting admixture may advantageously subsequently be sheeted to thicknesses ranging from 5 to 200 mils, sheet thicknesses generally ranging from about 35 to about 60 mils, utilizing conventional sheeting methods such as milling, calendering, or extrusion.

The commercial approach is to roll the sheeted membrane onto

curing mandrels, with a liner placed between the membrane plies, and curing in a steam autoclave. Alternatively, the sheet may be dusted with talc or mica, rolled upon itself on the curing mandrel, and cured in a steam autoclave.

The sheet could also be cured, without utilizing such a liner, by transporting the sheet through a heated oven, and the sheet subsequently cooled. After cooling, the sheet can be rolled up with a release liner for transport.

One preferred method of heat-seaming edge margins of cured, thermoplastic-containing sheet-like membranes of the present invention is described as follows. As a sheet is unrolled over a preselected surface such as a roof or other substructure in a conventional manner, the seams of adjacent sheet layers are overlapped.

The width of such an overlapped seam can vary considerably, depending upon various requirements specified by a particular architect or building contractor; and thus any such seam-overlap considerations do not constitute a limitation upon the claims of our present invention.

Assuming an overlap of several inches, the next step is to apply sufficient heat and pressure to the edge margins, to form the seams. The resultant seam area, consisting of overlapping edge margins of adjacent sheets, is preferably heated to the softening point of the sheet material.

Temperature is advantageously maintained at a value greater than the melting/softening temperature of the thermoplastic polymeric material while sufficient pressure is applied for a suitable period of time.

In one specific case we found that the seaming temperature had to be equal to or greater than the melting point of the HDPE utilized.

Numerous techniques which utilize heat and pressure can be used to produce an effective seam and are known to those skilled in the art. Pressure can vary widely from a minimum of about 3 psi up to about 60 psi, for as long as is necessary, for purposes of providing desired seam strength. In order to demonstrate utility of the present invention, several

EPDM sheeting compounds were prepared with varying amounts of high density polyethylene ("HDPE").

The resultant compositions-of-matter were subjected to peel adhesion testing at room temperature and at 70 °C, as well as tests which determined tensile properties, and trouser-tear properties.

The resultant compositions-of-matter of our present invention were prepared according to procedures set forth in detail below.

In order to keep the sheets separate, they may be wrapped-cured in liners of nylon, polyester, or other such material.

Talc or mica, usually used to separate such sheets, were not able to be used, as use of such would undesirably affect the ability of the thermoplastic-containing, cured sheets to achieve desired adhesion.

While our present invention is susceptible to embodiment in various forms, there is hereinbelow presented and detailedly described a number of examples which embody various principles of our present invention. The present disclosure, therefore, is to be considered as merely an exemplification or illustration of our present invention, without limitation to the specific embodiments or examples discussed herein.

<u>Examples 1 through 6</u>

Examples 1 through 6 illustrate thermoset roofing compositions of our present invention. These thermoset roofing compositions comprise blends of EPDM and high density polyethylene ("HDPE"). The following examples — which are illustrative of our present invention — have the following compositions and are prepared as set forth below.

In the following examples, blends of "Royalene" (brand) EPDM elastomer and HDPE, when cured in sulfur-compounded stock, were heat-seamed and the resulting samples tested at room temperature (i.e. 25 °C) and at the elevated temperature of 70 °C to determine peel adhesion.

To determine optimal level of adhesion properties, levels of HPDE were evaluated at 5 parts to 50 parts (Examples 2 through 6); and with the no HDPE formulation being evaluated as Comparative Example "A."

("Royalene" is a trademark of Uniroyal Chemical Company, Inc., of Middlebury, Connecticut.) Formulations are presented below in Table I.

Table I

Example No. or Comparative Experiment	A	1	2	3	4	5	6
EPDM, phr	100.0	100.0	100.0	100.0	100.0	100.0	100.0
HDPE, phr	0	5.0	10.0	20.0	30.0	40.0	50.0
N-650 Black, phr	125.0	125.0	125.0	125.0	125.0	125.0	125.0
Paraffinic Oil, phr	95.0	95.0	95.0	95.0	95.0	95.0	95.0
Zinc Oxide, phr	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid, phr	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Delac NS, phr	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Tuex, phr	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ethyl Tuex, phr	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur, phr	0.7	0.7	0.7	0.7	0.7	0.7	0.7

Notes for Table I:

(1) EPDM is "Royalene 3180," a Trademark of Uniroyal Chemical Co. Inc.

(2) HDPE is "Fortiflex T50-200", available from Solvay Polymers.

(3) N-650 Black is carbon black, Iodine No. 36, absorption no. 122.

(4) Paraffinic Oil is "Sunpar 2280", ASTM-D 2226, Type 104B.

(5) Zinc Oxide is "Kadox 720", French process.

(6) "Delac NS" is N-*tert*-butyl-2-benzothiazole sulfenamide, delayed action accelerator, a trademark of Uniroyal Chemical Company, Inc.

(7) "Tuex" tetramethylthiuram disulfide accelerator is a trademark of Uniroyal Chem. Co.

(8) "Ethyl Tuex" tetraethylthiram disulfide accelerator is also a trademark of Uniroyal.

(9) Sulfur is code 104, Rubbermaker's.

Formulation Procedures

The formulations of Table I were prepared by first mixing the EPDM, the HDPE, the N-650 carbon black, and the paraffinic oil ingredients in a "Brabender" Prepcenter (mixer) having a jacket temperature of 135 °C to form a masterbatch. The final mix temperature of this batch was 145-155 °C. The speed of the mixer was set at 50 revolutions per minute ("rpm").

The masterbatches were then mixed with the other ingredients including zinc oxide, stearic acid, Delac NS, Tuex, Ethyl Tuex, and sulfur in the Brabender Prepcenter mixer at a jacket temperature of 50 °C. The temperature of the mixed stock did not exceed 100 °C.

The stocks were then refined and sheeted out on a mill, the temperature of this also did not exceed 100 °C. The stocks were cured for 20 minutes at 160 °C in an ASTM mold having dimensions of 15 cm by 15 cm by 1.9 mm (6 in by 6 in by 0.075 in). The cured slabs were then used to prepare tensile-test samples, trouser-tear samples, and peel-adhesion samples. The resultant compounds were tested for stress-strain and peel adhesion properties after aging at 23 °C for 24 hours. Stress-strain samples were prepared and tested according to ASTM D 412-87, Method A. Peel adhesion samples were prepared at a cross-head speed of two (2) inches/minute according to the following method.

The adhesion pads were wiped with mineral spirits solvent (e.g. white gasoline, and the like). In field installations, the seam area is always washed with solvent to clean the surface of foreign material prior to applying an adhesive. The 6 in by 6 in slabs were cut in half, and the halves were next sandwiched together along with a 2.5 cm by 17.5 cm (1 in by 7 in) long Teflon spacer placed along the top edge.

The composite was subsequently placed between two additional Teflon sheets of similar dimension and next placed in a hot press which was set at 160 °C. The heated platens of the press were closed until both just touched the surface of the composite.

The sample was heated at 160 °C for 5 minutes. When removed from the press, the heat-joined section of the composite was rolled with a metal hand roller weighing 850 grams. The rolled composite was then cooled for one (1) hour, and the Teflon spacer subsequently removed. Thereafter, five (5) adhesion pad samples measuring 2.5 cm by 7.5 cm (1 in by 3 in) were cut from the composite.

Three of these samples were tested for 180-degree peel adhesion at room temperature and two samples were tested at 70 °C.

Table II

Example No. or Comparative Experiment	A	1	2	3	4	5	6
HDPE, phr	0	5.0	10.0	20.0	30.0	40.0	50.0
Peel Adhesion, pli, @ 23 °C	8	25	36	39	45	60	52
Peel Adhesion, pli, @ 70 °C	1	3	9	23	15	29	22
Tensile Strength, psi	1520	1500	1430	1350	1560	1650	1580
300% Modulus, psi	770	820	840	870	790	800	830
Elongation at Break, %	700	770	690	620	800	870	810
Trouser Tear, @ 23 °C	183	170	207	213	240	230	260

Notes for Table II:

(1) Example A is a comparative sample.

(2) Peel adhesion samples were tested at 2 inches per minute.

(3) ASTM D412-87, Method A.

(4) Trouser Tear, ASTM D-1938-85.

General Comments

Greater "pli" values indicate stronger adhesion. Tensile strength and trouser tear are important properties associated with sheeting membranes. ASTM-D 4637 stipulates that an EPDM non-reinforced membrane must have a minimum tensile strength of 1305 psi. The membranes which are the subject of the instant invention, including those used in single ply non-reinforced roofing, are in this category.

Conclusions

As shown in the above examples (Table II), all of the membranes containing HDPE (Examples 1 through 6) are higher in peel adhesion when tested at 23 °C and 70 °C, as compared to Comparative Example A.

The preceding examples have led to an optimization of the level of high density polyolefin to the EPDM and other ingredients used herein. No negative impact on trouser tear at room temperature was observed in the formulations using HDPE for adhesion promotion. Tensile strength and tear resistance (Trouser Tear) are important properties associated with sheeting membranes; and Examples 1 through 6 show that the addition of HDPE does not detract from either of these properties, when compared to Comparative Example A.

Examples 7 through 8

Examples 7 through 8 illustrate the importance that mixing temperature plays, when maximizing heat-seamable peel adhesion values.

In relation to Examples 7 and 8, the same formulation was used as in Example 2, with the exception of the type of HDPE used, mixed at the temperatures presented in Table III.

Table III		
Example No.	7	8
Masterbatch mix temp, °C	145	95
Peel Adhesion, pli @ 23°C	42	20
Peel Adhesion, pli @ 70°C	6	2
Tensile Strength, psi	1550	1560
300% Modulus, psi	710	750
Elongation at Break, %	830	810
Trouser Tear @ 23°C	210	230

Notes for Table III:

(1) The high density polyethylene used in Examples 7 and 8 was "Microthene MA 795-00," a high density polyethylene powder, rotational molding grade, having a melt index of 5.0, a density of 0.946 and a flexural modulus (1 % secant) of 117,250 psi, available from USI Chemicals Co. of Cincinnati, Ohio.

(2) The amount of HDPE used in Examples 7 and 8 was 10.0 phr.

General Comments

The higher value of peel adhesion at a masterbatch mixing temperature is evidence of the need to mix the HDPE into the formulation at or above the crystalline melting temperature. Even though the HDPE used in Example 8 was a fine powder, it formed a grainy appearance on the surface of both the uncured and cured samples, presenting an unsightly appearance which might preclude use in many fabricated rubber articles.

Examples 9 Through 12

The following examples, prepared using procedures set forth above, indicate that other grades of polyethylene besides FORTIFLEX T50-200 can be used in this invention.

The heat of fusion (J/gm) and melting point (m.p.) data presented in Table IV below were obtained from Differential Scanning Calorimeter ("DSC") melting transition curves, from procedures performed in our laboratory.

The standard method for calculating crystallinity is to compare a particular J/gm value with that of a very crystalline PE. Polyethylene at near 100 % crystallinity has a Heat of Fusion value of 277-280 J/gm, as reported in the POLYMER HANDBOOK. When the J/gm value of each polymer is divided by the value 279 J/gm, the quotient when multiplied by 100 becomes the percent crystallinity value, as based upon the 100 % crystalline PE standard. Our preferred DSC crystallinity determining procedure is set forth hereinbelow.

Table IV

Example No.	9	10	11	12
Identification	FORTIFLEX T50-200	EXXON 1001.9	AC617A	FLEXOMER GRS 1085
PE Type	HDPE	LLDPE	LOW MW PE	REACTOR TPO
J/gm	200	116	105	52
m.p.,°C	133	122	96	121
% Cryst.	72	42	38	19
Loading, phr	20	10	20	20
Peel Adhesion @ RT, pli	55	30	32	49

Notes for Table IV: (1) EXXON (brand) polyolefins are available from Exxon Corporation, which has a business office in Irving, Texas, United States of America (U.S.A.); (2) AC617A (brand) polyethylene is available from R.T. Vanderbilt of Norwalk, Connecticut, U.S.A. and (3) FLEXOMER (brand) polyolefins are available from Union Carbide, of New York, New York, U.S.A.

Procedure For Differential Scanning Calorimeter Analysis of EPDM Rubber

(1) Mold sample into a rectangular plaque, using a mold which is 40 mm by 50 mm by 0.6 mm. Mold for fifteen (15) minutes at 150 °C (302 °F), and then water cool. Use 20,000 pounds force for molding.

(2) After molding, allow sample to set at least twenty-four (24) hours at room temperature.

(3) Die-cut two (2) ca. 6 mm-diameter specimens from the molded plaque; place sample in a tared aluminum pan; and weigh specimen. Each sample should weigh about 25 mg.

(4) Secure a crimpable cover over each sample pan.

(5) Place the sample(s) into the dry box attached to the DSC.

(6) Calibrate the DSC instrument (Perkin Elmer DSC-7) with Indium and Octane. After calibrating, the instrument reproducibility should be in the following range:

Indium: Onset = 156.6 $\pm$ 0.5 °C , DH_f = 28.5 $\pm$ 0.5 J/G

Octane: Onset + -56.76 $\pm$ 0.5 °C.

(7) Place the sample pan in the sample holder; and use an empty reference pan in the reference side.

(8) Using liquid nitrogen as coolant, cool the sample to -100 °C.

(9) When the baseline is no longer changing, begin the scan.

(10) Scan from -100 °C to +200 °C at 20 °C per minute. Record the curve.

(11) Bring the sample to 30 °C and remove.

Seaming Conditions

FORTIFLEX T50-200 at a 20 phr recipe loading, prepared in accordance with the recipe set forth in Examples 1-6 (Tables I and II), was evaluated at various heat-seaming temperatures, and is set forth

below in Table V. All of the adhesion data illustrated by the examples set forth in this specification, except for what is set forth in Table V, resulted from the seaming conditions of five (5) minutes @ 160 °C (320 °F).

Conclusions: The data show that excellent adhesion results are possible at reduced seaming conditions of as little time as only thirty (30) seconds, and at a temp. of 135 °C (275 °F). Such less-demanding conditions would prove to be more favorable under typical field seaming conditions.

Table V

Seaming Conditions	Peel Adhesion @ RT, pli
5 minutes @ 160 °C	42
60 seconds @ 160 °C	54
30 seconds @ 160 °C	51
30 seconds @ 135 °C	57
30 seconds @ 121 °C	14

What has been described herein is a novel method for making a thermoplastic-containing, cured elastomeric matrix.

While our present invention has been described with reference to certain preferred embodiments, it is to be understood that the scope of our present invention is not to be limited to these specific examples.

On the contrary, various alternatives, changes, and modifications will become readily apparent to those skilled in the art upon reading our foregoing specification. Accordingly, any such alternative, change or modification is to be considered as forming a part of our invention insofar as such falls within the spirit and scope of the accompanying claims.

We claim:

1. A method for producing a thermoplastic-containing, vulcanizable elastomeric matrix, comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix.

2. A thermoplastic-containing, vulcanizable elastomeric matrix produced by a method, the steps of the method comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the

elastomeric material, thereby producing the thermoplastic-containing, vulcanizable elastomeric matrix.

3. A method of producing a thermoplastic-containing, heat-seamable, vulcanized elastomeric matrix, comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, heat-seamable, vulcanizable elastomeric matrix, and

(3) subsequently subjecting the vulcanizable elastomeric matrix to heat and pressure sufficient to cure the matrix, thereby producing a thermoplastic-containing, heat-seamable, vulcanized elastomeric matrix.

4. A thermoplastic-containing, heat-seamable, vulcanized elastomeric matrix produced by a method, the steps of the method comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, heat-seamable, vulcanizable elastomeric matrix, and

(3) subsequently subjecting the vulcanizable elastomeric matrix to heat and pressure sufficient to cure the matrix, thereby producing a thermoplastic-containing, heat-seamable, vulcanized elastomeric matrix.

5. A method for producing a thermoplastic-containing, vulcanizable elastomeric membrane, comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix, and

(3) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane.

6. A thermoplastic-containing, vulcanizable elastomeric membrane, produced by a method, the steps of the method comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix, and

(3) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane.

7. A method for producing a thermoplastic-containing, vulcanized elastomeric membrane, comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic

polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix,

(3) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane, and

(4) curing the membrane.

8. A thermoplastic-containing, vulcanized elastomeric membrane, produced by a method, the steps of the method comprising:

(1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix,

(3) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane, and

(4) curing the membrane.

9. A method of joining together edge margins of separate sheets of cured, thermoplastic-containing elastomeric membrane material, comprising:

(1) producing a first thermoplastic-containing, vulcanizable elastomeric membrane by

(a) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(b) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix, and

(c) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane,

(2) producing a second thermoplastic-containing, vulcanizable elastomeric membrane by repeating the above,

(3) curing the first and second thermoplastic-containing, vulcanizable elastomeric membranes,

(4) overlappingly contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes, and

(5) subjecting the overlappingly contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes to heat and pressure sufficient to bond the contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes together, for purposes of providing a water-tight joint therebetween.

10. A heat-seamed, thermoplastic-containing, vulcanized elastomeric matrix, produced by a method, the steps of which comprise:

(1) producing a first thermoplastic-containing, vulcanizable elastomeric membrane by

(a) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while

(b) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a thermoplastic-containing, vulcanizable elastomeric matrix, and

(c) subsequently forming the thermoplastic-containing, vulcanizable elastomeric matrix into a membrane,

(2) producing a second thermoplastic-containing, vulcanizable elastomeric membrane by repeating the above,

(3) curing the first and second thermoplastic-containing, vulcanizable elastomeric membranes,

(4) overlappingly contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes, and

(5) subjecting the overlappingly contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes to heat and pressure sufficient to bond the contacting edge margins of the first and second thermoplastic-containing, vulcanized elastomeric membranes together, for purposes of providing a water-tight joint therebetween, thereby producing a heat-seamed, thermoplastic-containing, vulcanized elastomeric matrix.

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(57) Abstract

Disclosed is a method for producing a heat-seamable, thermoset elastomeric matrix, the method comprising: (1) combining a vulcanizable elastomeric material and a thermoplastic polymeric material having a predetermined softening/melting temperature, in a manner so as to produce a dispersion of the thermoplastic polymeric material throughout the vulcanizable elastomeric material, while (2) heating the dispersion at a temperature above the softening/melting temperature of the thermoplastic polymeric material, in a manner and for a period of time sufficient to enable the thermoplastic polymeric material to soften or melt and become dispersed throughout the elastomeric material, thereby producing a vulcanizable elastomeric matrix, and (3) curing the thermoplastic-containing matrix, thereby producing the heat-seamable, thermoset elastomeric matrix.

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,33 16 302 (METZELER KAUTCHOUK) 8 November 1984 see page 4, line 14 - line 27; claims 1,3 ---	1-10
X	US,A,4 722 961 (B. TOPCIK) 2 February 1988 see column 3, line 1 - line 11; claim 1 see column 4, line 3 - line 55 ---	1-10
Y	EP,A,0 143 131 (BRIDGESTONE TIRE COMPANY; MITSUI PETROCHEMICAL INDUSTRIES) 5 June 1985 cited in the application see claims 1,5 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 242 727 (B.J. BRIDDELL ET AL) 7 September 1993 see abstract see column 3, line 10 - line 50 see column 6, line 14 - line 37 -----	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

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